

CLAIMS

What is claimed is:

1. A process of preparing ortho substituted phenylamines comprising contacting phenylhydroxylamine, optionally substituted with at least one inert substituent, with a nucleophilic reagent in the presence of a manganese oxide at a temperature between about 10° C and about 170° C and a pressure from subatmospheric to superatmospheric such that an ortho substituted phenylamine, optionally correspondingly substituted with at least one inert substituent, is predominantly formed.
2. The process of claim 1 wherein the phenylhydroxylamine is unsubstituted phenylhydroxylamine.
3. The process of claim 1 wherein the phenylhydroxylamine is substituted with at least one member selected from the group consisting of C₁-C₁₀ alkyl, C₆-C₁₀ aryl, and C₆-C₁₀ alkaryl moieties.
4. The process of claim 1 wherein the nucleophilic reagent is selected from the group consisting of ammonia, water, C₁-C₂₀ aliphatic alcohols, phenols, halides, and amines having the formula R'₂NH wherein each R' may independently be a hydrogen, C₁-C₂₀ aliphatic, C₄-C₈ alicyclic, or C₆-C₁₅ aryl or alkaryl moiety.

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5. The process of claim 1 wherein the nucleophilic reagent is an amine represented by the formula R'_2NH wherein each R' is independently a hydrogen, C_1 - C_5 alkyl, or C_6 - C_{10} phenyl or alkyl-substituted phenyl moiety.

5 6. The process of claim 5 wherein the nucleophilic reagent is aniline.

7. The process of claim 1 wherein the molar ratio of nucleophilic reagent to phenylhydroxylamine ranges from about 2 to about 100.

10 8. A process for preparing ortho substituted phenylamines comprising contacting phenylhydroxylamine, optionally substituted with at least one inert substituent, with a nucleophilic reagent, the molar ratio of nucleophilic reagent to phenylhydroxylamine ranging from about 2 to about 100, the contacting of the phenylhydroxylamine and nucleophilic reagent being conducted in the absence of oxygen and in the presence of a catalyst that is a
15 cryptomelane-type manganese oxide Octahedral Molecular Sieve, with a composition of $KMn_8O_{16} \cdot nH_2O$ ($n = 0.5-10$) in which said molecular sieve comprises MnO_6 octahedral structural units that are edge and corner shared to form a 4.6×4.6 tunnels as a result of 2×2 arrangement of octahedra, in which the potassium ions are present in the tunnels with a small amount of water and said potassium ions are ion-exchanged by H^+ ions using nitric acid to
20 obtain the acidic form of said sieve at temperatures ranging from about $70^\circ C$ to about $120^\circ C$, whereby an optionally-substituted ortho substituted phenylamine is formed in amounts equal to or greater than any concurrently formed para isomer.

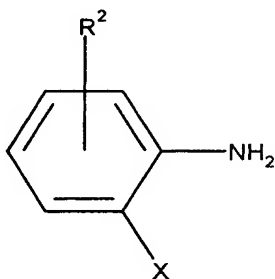
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9. The process of claim 8 wherein the phenylhydroxylamine is unsubstituted phenylhydroxylamine.

10. The process of claim 8 wherein the nucleophilic reagent is selected from the group consisting of ammonia, water, C₁-C₂₀ aliphatic alcohols, phenols, halides, and amines having the formula R'₂NH wherein each R' may independently be a hydrogen, C₁-C₂₀ aliphatic, C₄-C₈ alicyclic, or C₆-C₁₅ aryl or alkaryl moiety.

11. The process of claim 8 wherein the nucleophilic reagent is aniline.

12. The process of claim 8 wherein the ortho substituted phenylamine is represented by the formula:



wherein R² is hydrogen or at least one C₁-C₁₀ alkyl moiety, and X is selected from hydroxy, halo, C₁-C₂₀ alkoxy, phenoxy, and amino of the formula -NR'₂ wherein each R' is independently a C₁-C₂₀ aliphatic, C₄-C₈ alicyclic, or C₆-C₁₅ aryl or alkaryl moiety.

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13. The process of claim 12 wherein X is amino and the ortho substituted phenylamine is a o-phenylenediamine.

14. The process of claim 13 wherein the ortho substituted phenylamine is o-

5 aminodiphenylamine represented by the formula:

